

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

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In re application of: Wu et al.

Attorney Docket No.:  
NOVLP094/NVLS-2919

Application No.: 10/789,103

Examiner: Bret P. Chen

Filed: February 27, 2004

Group: 1762

Title: METHODS FOR PRODUCING LOW-K  
CDO FILMS WITH LOW RESIDUAL STRESS

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***DECLARATION UNDER 37 CFR § 1.132***

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Dear Sir:

I, Qingguo Wu declare as follows:

1. I joined Novellus Systems, Inc., assignee of the above-identified patent application, as a scientist in 2002. Prior to joining Novellus, I worked in the Department of Chemical Engineering at the Massachusetts Institute of Technology as a postdoctoral associate for 2 years. I received a Ph.D. in Materials Chemistry from Queen's University, Canada in 2000 and a M.S. in Electrochemistry from Henan University, China in 1990. I was a visiting scientist and worked in the Department of Chemistry at Cornell University for 2 years before joining Professor Suning Wang's group at Queen's University in 1997. I have authored or coauthored more than 50 publications in refereed journals and am an inventor on 4 patents and 9 patent applications. My research efforts include the research and development of low-k dielectrics, low-k barrier and high stress nitride materials. I also research film process optimization to address the integration and reliability issues in early development stage.
2. I am the inventor of the subject matter described and claimed in the above-identified patent application. The patent application describes and claims methods of depositing carbon-doped oxide films having low stress and low dielectric constant.
3. I have extensive experience in depositing and evaluating carbon doped oxide films. At Novellus, I have over the past few years been involved with or directed the

deposition of hundreds of carbon doped oxide films. I have evaluated the chemical and mechanical properties of these films according to standard protocols employed in the field.

4. Stress related problems are pervasive and critical in Cu-low k integration. Many device failures can be ultimately traced to stresses and their variations at various stages of IC processing. Those failures include interfacial delamination between different materials and cracking within one material during chemical mechanical polishing (CMP) and packaging.
5. We found in our work that both using a triple bond-containing precursor and using a dual source electrode with different frequencies to deposit a CDO film from a triple bond-containing precursor are critical in obtaining films with low dielectric constant and low magnitude of stress.
6. We found in our work that low frequency power is critical factor for obtaining low film stress. Specifically we found that stress decreases with increasing low frequency power percentage [LF/(LF+HF), %]. This is shown in Appendix A (Figure 10 from our application), which shows stress as a function of low frequency power percentage for low-k CDO films deposited using TMSA and a carbon dioxide carrier gas. It is believed that the low frequency (LF) RF power is effective in modulating the concentration of the -C≡C- desired bonds to modulate the residual stress accordingly. Based on the data in Figure 10, I would expect a single frequency process (LF power is zero) would result in a residual stress of greater than about 40 MPa for a low-k CDO film deposited with TMSA (ETMS) with similar conditions. The data in Appendix B indicates that films deposited with unsaturated precursors using single frequency power have fewer -C≡C- bonds and higher residual stress than films deposited with dual frequency power. It also shows that dual frequency processes are critical to obtaining films with low residual stress.
7. We also found in our work that film compressive stress is proportional to the Si-CH<sub>3</sub> group concentration of a precursor. In particular, a precursor with several Si-CH<sub>3</sub> groups and a C≡C group produces the highest compressive stress in the high-k range (k > 3.0) or lowest tensile stress in the low-k range. This is shown in Appendix B, which shows stress as a function of dielectric constant for different precursors with specific functional groups. In the range of k < 3.0, only the precursors having several Si-CH<sub>3</sub> groups and a C≡C group have a stress with a magnitude less than 0 MPa (compressive stress).

8. Low frequency power is also critical for obtaining high cracking threshold. Attached in Appendix C is a direct comparison of FTIR spectra for film A from a single frequency process (HF power 1400 W) and film B from a dual frequency process (HF power 1200 W and LF power 200 W). Films were deposited using TMSA. Both films exhibit an absorption peak corresponding to C-H stretch around 2900 to 3000  $\text{cm}^{-1}$ . The peaks around 1250-1280  $\text{cm}^{-1}$  in the FTIR spectra were assigned to  $\text{Si-(CH}_3\text{)}_x$  methyl rocking bands at 1273 and 1263  $\text{cm}^{-1}$ , respectively. The peak around 1350-1375  $\text{cm}^{-1}$  is due to  $\text{Si-CH}_2\text{-Si}$  bands (see the inset of Figure 1), the intensity of which indicates the degree of cross-linking of methyl groups in the OSG film. It is observed that film B obtained from the dual frequency process have a significantly higher content of cross-linking bonds than film A obtained from the single frequency process does. The data shown in this graph is representative of data have obtained in other experiments. Film B also had a much higher cracking threshold than film A: a cracking threshold of 4.2  $\mu\text{m}$  was measured for film B and 1.5  $\mu\text{m}$  for film A. This indicates that film B has much more cross-linking bonds than film A. The data in Appendix C indicates that films deposited with unsaturated precursors using single frequency power will have less cross-linking bonds and low cracking threshold. It also shows that dual frequency processes are critical to  $\text{Si-CH}_2\text{-Si}$  cross linking bonds and that  $\text{Si-CH}_2\text{-Si}$  cross linking bonds are critical to obtain high cracking threshold films.
9. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true. I further declare that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both (under Section 1001 of Title 18 of the United States Code), and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.



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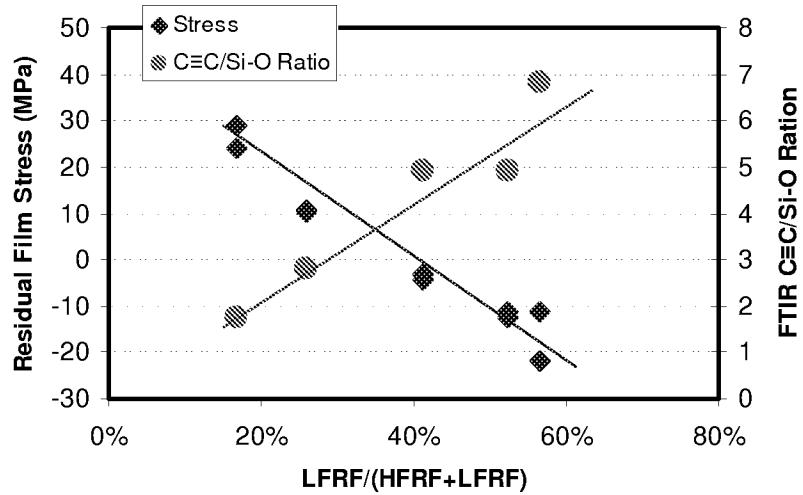
Qingguo Wu

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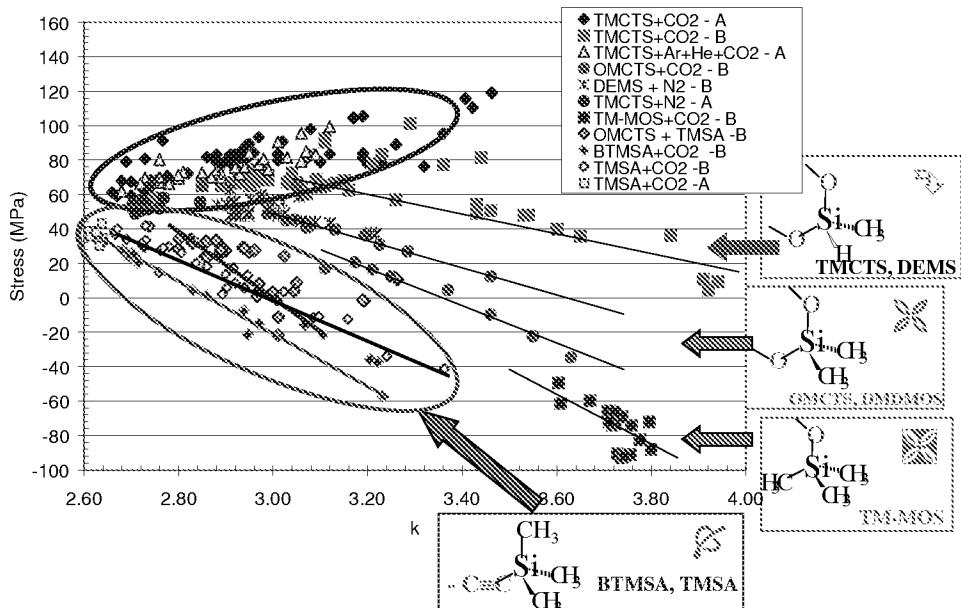
## Appendix A

Residual film stress and FTIR C≡C/Si-O ratio as a function of LFRF power percentage for a TMSA film (Figure 10)



## Appendix B

Stress as a function of dielectric constant for different precursors with specific functional groups.



## Appendix C

FTIR spectra of Film A from single frequency process and of Film B from dual frequency process.

